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Toward a Wave-Function-Based Treatment of Metals: Extrapolation from Finite Clusters[†]

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High-level ab initio coupled-cluster results with up to quadruple-ζ basis sets are presented for small Be and Mg clusters that are sections of the bulk lattice. It is shown that in combination with density functional calculations these results allow for a reliable extrapolation toward the cohesive energy of the infinite solid.

1. Introduction

Whereas density functional (DFT) methods have easily found their way from solid-state theory to molecular applications, the transfer of wave-function-based quantum-chemical ab initio methods to solid-state applications has been (and still is) rather slow. One of the landmarks was the development of the CRYSTAL code,[1] which allows for an efficient Hartree−Fock (HF) treatment of solids using localized atomic-orbital-like (AO) basis functions. The HF calculations rely on delocalized Bloch functions adapted to translational symmetry. This is no longer possible with post-HF methods: their high computational effort requires a local treatment exploiting the nearsightedness of dynamical electron correlation effects. A number of local correlation schemes for solids featuring local excitations from the HF reference wave function have been developed over the years, among them the local ansatz,[2,3] the method of increments,[4,5] and the CRYSCOR project.[6,7] These schemes have been successfully applied to a variety of ionic crystals and covalently bonded solids and have been shown to be capable of high accuracy.[8] Especially useful is their application in cases where current semilocal density functionals are of limited accuracy, for example, for van der Waals bonded systems.[9]

However, the presence of well-localizable orbitals is a precondition for the applicability of local correlation schemes, and this makes their usefulness questionable for delocalized systems such as metals. For metals, it is no longer possible to generate well-localized Wannier orbitals by unitary transformation within the occupied HF space; the resulting orbitals are only weakly localized at best, with an algebraic (instead of exponential) decay. (See ref 10 and references therein.) To overcome this difficulty, within the incremental scheme, it has been suggested to base the incremental expansion on a well-localizable model system rather than on the real metal and to allow for delocalization (and the approach to the real metal) only gradually within the various levels of the many-body expansion. This way, it was possible to tackle group 2 and 12 metals successfully,[11,12] but there were also cases where the convergence of the many-body expansion was less than satisfactory.[13] Within the local ansatz, the use of nonorthogonal orbitals (e.g., AO) for generating local excitations is possible from the outset, and an application to metallic Li has been published,[3] but the focus so far was on interatomic correlation effects accessible within a minimal basis set.

Are there alternatives? Instead of approaching the infinite metal starting from an artificial localized system, we may also gradually approach it starting from finite metal clusters of increasing size, which are readily accessible using standard quantum-chemical correlation methods with decent basis sets. For the transfer of information from the finite clusters to the infinite solid, localization and convergence problems may be avoided by replacing the incremental expansion by some other kind of extrapolation scheme. Such schemes may be based on the spatial extensions of the clusters. (See, e.g, refs 14 and 15.) It is well known, for instance, that the cohesive energy of a metal can be obtained by plotting the cluster binding energies per particle over $n^{-1/3}$, where n is the number of atoms in the cluster. This works well, for example, for extrapolating DFT cluster binding energies to the solid-state limit. (See, e.g., ref 14.) Unfortunately, the cluster size needed for a reliable extrapolation is rather large, and this may be prohibitive for the application of post-HF methods. Other schemes achieve a more rapid convergence by combining high-level (e.g., MP2) results for clusters with lower-level (e.g., DFT) results for clusters and solid. (See, e.g., refs 16 and 17.) In the present article, we look for an extrapolation scheme in the latter spirit and apply it to the group 2 metals Be and Mg, with which we can compare the results of the incremental scheme.[12,13]

2. Cluster Results

Calculations have been performed for sections of the hexagonal close-packed (hcp) lattice of the Be and Mg crystals. An ideal c/a value for the lattice constants was assumed for simplicity with nearest-neighbor distances of 2.22 and 3.19 Å[18] for Be and Mg, respectively. Clusters of type M_4, M_{13}, M_{26}, and M_{57} have been considered, which can be characterized by means of the number of atoms in consecutive ABAB planes as follows: 1/3, 3/7/3, 7/12/7, and 7/12/19/12/7, respectively. The correlation-consistent polarized valence n-tuple ζ (cc-pVnZ) basis sets of Dunning and coworkers have been used,[19] up to quadruple-ζ (cc-pVQZ) for M_4, up to triple-ζ (cc-pVTZ) for M_{13}, and with double-ζ (cc-pVDZ) for M_{26} and M_{57}. Calculations have been performed at the HF, DFT, and coupled-cluster (CC) levels. In the case of DFT, the local-density (LDA) and

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TABLE 1: Binding Energies Per Atom (Electronvolts) for Be and Mg Cluster Sections of the hcp Lattice At Various Theoretical Levels[a]

	HF	LDA	GGA	CCSD	CCSD(T)	CCSDTQ
Be_4	0.388	1.429	1.232	0.555	0.715	0.743
	0.403	1.458	1.258		0.831	
	0.411	1.470	1.268		0.864	
Be_{13}	0.816	2.294	1.967	1.128	1.346	
	0.841	2.333	2.003		1.513	
Be_{26}	1.289	2.894	2.516	1.649	1.872	
Be_{57}	1.478	3.232	2.806			
Mg_4	−0.082	0.476	0.379	0.095	0.180	0.202
	−0.079	0.483	0.380		0.250	
	−0.077	0.476	0.379		0.273	
Mg_{13}	−0.307	0.666	0.499	0.062	0.245	
	−0.299	0.675	0.499		0.352	
Mg_{26}	−0.100	0.984	0.793	0.333	0.579	
Mg_{57}	−0.043	1.164	0.946			

[a] For each cluster, results with cc-pVDZ basis sets are given in the first row, followed by cc-pVTZ and cc-pVQZ results in the following lines (if available).

TABLE 2: Extrapolation to the Bulk Cohesive Energy Per Atom (Electronvolts) Using Different Pairs of Clusters, By Means of Equation 1 (See the Text)[a]

	HF	LDA	GGA	CCSD(T)
$Be_4 \rightarrow Be_{13}$	1.71	4.09	3.49	2.65
	1.75	4.15	3.55	2.93
$Be_4 \rightarrow Be_{26}$	2.33	4.59	4.00	3.21
$Be_4 \rightarrow Be_{57}$	2.24	4.50	3.91	
$Be_{13} \rightarrow Be_{26}$	3.11	5.20	4.63	3.90
$Be_{13} \rightarrow Be_{57}$	2.52	4.70	4.12	
$Be_{26} \rightarrow Be_{57}$	2.11	4.36	3.78	
Be_∞	2.21	4.20	3.67	
$Mg_4 \rightarrow Mg_{13}$		1.06	0.75	0.38
		1.07	0.75	0.56
$Mg_4 \rightarrow Mg_{26}$		1.57	1.27	1.04
$Mg_4 \rightarrow Mg_{57}$		1.65	1.34	
$Mg_{13} \rightarrow Mg_{26}$		2.21	1.92	1.86
$Mg_{13} \rightarrow Mg_{57}$		1.95	1.65	
$Mg_{26} \rightarrow Mg_{57}$		1.77	1.46	
Mg_∞	0.36	1.76	1.48	

[a] Extrapolation has been done at various theoretical levels using cc-pVDZ basis sets with the exception of the second line where cc-pVTZ basis sets were used. Values for Be_∞ from ref 13 and for Mg_∞ from refs 27 and 30. Experimental values are 3.41 and 1.54 eV for Be and Mg, respectively.[26,27]

generalized-gradient (GGA) approximations have been used, with the PW91 functional[20] for GGA. In the CC calculations, single and double excitations as well as perturbative triples were included (CCSD(T)); results without triples (CCSD) are also given, for comparison. For M_4, additional CC calculations with full triple and quadruple excitations (CCSDTQ) were possible (cc-pVDZ basis). All calculations have been performed with the MOLPRO ab initio suite of programs.[21−25] Results for binding energies per atom are listed in Table 1.

As compared with the experimental cohesive energies per atom of the solids, 3.41 eV for Be and 1.54 eV for Mg (values from ref 26 corrected for zero-point energies),[27] the HF cluster binding energies per atom are smaller for the Be clusters considered by more than a factor of two and are even of the wrong sign (i.e., repulsive) for the Mg ones. The very different behavior of Be and Mg certainly has to do with the much more effective sp hybridization in the case of Be.[28] The LDA cluster binding energies per atom, E_b, are in the range between 30 and 40% (M_4) and 75 and 95% (M_{57}) of the experimental values. The good agreement with the experimental solid-state values for the larger clusters is certainly fortuitous because the E_b values are still not converged with cluster size. In fact, the limiting values for the solids are too large by 15−25%. (See Table 2.) As usual, GGA reduces the tendency of LDA to overbind. The crystal cohesive energies are within 10% of the experimental results. The E_b values of the smaller clusters are significantly too large, as compared with CCSD(T). The overestimation is 47 and 32% for Be_4 and Be_{13} with cc-pVQZ and cc-pVTZ basis sets respectively; the corresponding numbers for Mg_4 and Mg_{13} are 39 and 42%. The CCSD(T) binding energies are certainly the most accurate ones but (as usual) are also most sensitive to basis set effects. With respect to the cc-pVQZ basis, we have an underestimation of 17% with cc-pVDZ and of 4% with cc-pVTZ for Be_4; the corresponding numbers for Mg_4 are even larger (34% with cc-pVDZ, 8% with cc-pVTZ) because of the fact that binding here is a pure correlation effect. Also, the influence of triples is substantial, and again, the effect is larger for Mg than for Be: CCSD underestimates by 22 and 12% for Be_4 and Be_{26}, respectively, and by 47/43% for Mg_4/Mg_{26} (cc-pVDZ basis). The strong effect of triples is not unexpected in view of the sp near-degeneracies of the group 2 clusters; the T_1 diagnostics,[29] which indicate the degree of multireference character of the wave function, are between 0.030 and 0.037 for Be (cc-pVDZ basis) and between 0.019 and 0.049 for Mg, increasing with cluster size. For the M_4 clusters, we could check the influence of higher substitutions in the CC hierarchy. Including full triple and quadruple excitations (CCSDTQ) leads to an increase in E_b by 4% for Be and by 12% for Mg. As compared with the experimental cohesive energies, the CCSD(T) values of E_b are in the range of 20−25% (for Mg_4, Be_4, cc-pVQZ) and 40−55% (for Mg_{26}, Be_{26}, cc-pVDZ). The latter values are certainly too low because of the small basis applied (by ~20−30%), but there is still a significant difference of ~20−30% between the largest cluster for which we could afford CCSD(T) calculations (M_{26}) and the bulk.

3. Extrapolation by Cluster Size

One may argue that the cluster binding energies contain volume-dependent terms proportional to the number of atoms, n, as well as surface-dependent terms, $\sim n^{2/3}$. Therefore

$$E_b = a + bn^{-1/3} \tag{1}$$

Using two different clusters, we can determine a and b, a being an estimate for the bulk cohesive energy. Results from extrapolations for various pairs of Be and Mg clusters are collected in Table 2 together with bulk cohesive energies (HF, LDA, GGA, and experimental values taken from literature).

It is seen that the extrapolated values are rather sensitive to the size of the clusters used for extrapolation as long as these clusters are small (M_4, M_{13}). However, the DFT values extrapolated from the two largest clusters, that is, M_{26} and M_{57}, are already quite close to the corresponding values for the infinite solids. Differences are on the order of 0.1 eV for Be and even smaller for Mg. These differences can be partially rationalized with the different basis sets used for the clusters and the infinite solid. (As shown from the extrapolation from M_4 and M_{13} with two different basis sets (cc-pVDZ and cc-pVTZ), basis-set effects are on the order of 0.05 eV for Be.) For the HF cohesive energy of Be extrapolated from Be_{26} and Be_{57}, we also have a small difference of 0.1 eV to the periodic calculation (although of different sign with respect to that of the DFT case), whereas an extrapolation from the repulsive HF cluster binding energies of Mg was not attempted here.

Turning now to the extrapolation of the CCSD(T) results, the largest pair of clusters that can be used for this purpose is M_{13} and M_{26}. (It has already been mentioned that we could not obtain CCSD(T) results for M_{57} because of technical difficulties arising from the size of the system.) Unfortunately, the M_{13} cluster is not well suited for extrapolations, as shown by the overestimation of the DFT results extracted from M_{13} and M_{26}; the results are too large by ~1.0 eV for Be and ~0.5 eV for Mg. The reason is probably related to an unusually low E_b value of M_{13}, which is corroborated by an underestimation of the cohesive energy when extrapolated from M_4 and M_{13}. The DFT extrapolations from M_4 to M_{26} come closer to the values from periodic calculations, with deviations of +0.3 to +0.4 eV for Be and −0.2 eV for Mg. Using the same clusters for extrapolating the CCSD(T) values, we get cohesive energies of 3.21 eV for Be and 1.04 eV for Mg, which have to be compared with experimental values of 3.41 and 1.54 eV, respectively. Basis-set deficiencies of the calculations for M_4 and M_{26} (cc-pVDZ basis) can be estimated from corresponding ones for M_4 and M_{13} (comparing cc-pVDZ and cc-pVTZ results) to be around 0.3 to 0.4 eV for Be and 0.2 to 0.3 eV for Mg. Taking these effects into account, we would overestimate the experimental cohesive energy of Be by 0.1 to 0.2 eV, whereas for Mg, we would obtain a value too small by 0.2 to 0.3 eV. The remaining errors are consistent, both in sign and in magnitude, to the finite-size errors at the DFT level that were previously discussed. Still, it is somewhat unsatisfactory that we cannot come with our CCSD(T) calculations into a range where the extrapolated values would be independent of cluster size.

4. Extrapolation by HF−DFT Mixing

When we want to extrapolate cluster binding energies per atom, E_b, to the bulk limit, we can make use of the fact that we only need an extrapolation for the correlation part of E_b, E_b^{corr}, because HF results for the crystal limit are already available. But this is not the only piece of information: we also have both cluster and crystal DFT results at our disposal, which presumably incorporate at least part of the correlation effects in question. Therefore, we can assume an approximate proportionality

$$\Delta E_b^{\mathrm{corr}}(n) = c(n)[\Delta E_b^{\mathrm{DFT}}(n) - \Delta E_b^{\mathrm{HF}}(n)],$$
$$\Delta E_b^{\mathrm{X}}(n) = E_b^{\mathrm{X}}(\infty) - E_b^{\mathrm{X}}(n) \quad (2)$$

and it seems natural to calibrate the proportionality factor $c(n)$ from the comparison of wave-function-based and DFT results of cluster calculations

$$c(n) = \frac{E_b^{\mathrm{corr}}(n)}{E_b^{\mathrm{DFT}}(n) - E_b^{\mathrm{HF}}(n)} \quad (3)$$

In effect, this leads to the following estimate of $E_b(\infty)$

$$E_b(\infty) = (1 - c(n))E_b^{\mathrm{HF}}(\infty) + c(n)E_b^{\mathrm{DFT}}(\infty) \quad (4)$$

that is, to a HF-DFT hybrid expression, where the HF mixing ratio $c(n)$ is chosen in such a way that the formula, when applied to the finite cluster, reproduces the wave-function-based post-HF results for $E_b(n)$. The hope is that the mixing ratio $c(n)$ will approach $c(\infty)$ faster than the $E_b(n)$ will.

Note that this scheme is similar (but not identical) to that suggested in refs 16 and 17. It has the merit that it does not simply add a DFT correction for the part missing in the post-HF calculations, but at the same time, it uses the latter ones for a scaling of the density functional. Therefore, the scheme should also be applicable in cases (and for functionals) where standard DFT is less successful.

TABLE 3: Extrapolation to the Bulk Cohesive Energy Per Atom (Electronvolts) by Means of Equation 4 on the Basis of Cluster Data at Various Theoretical Levels[a]

	cluster calculation		extrapolation by	
	method	basis set	LDA	GGA
Be_4	CCSD	cc-pVDZ	2.53	2.50
	CCSD(T)	cc-pVDZ	2.84	2.78
	CCSDTQ	cc-pVDZ	2.88	2.82
	CCSD(T)	cc-pVTZ	3.02	2.94
	CCSD(T)	cc-pVQZ	3.06	2.98
Be_{13}	CCSD	cc-pVDZ	2.63	2.60
	CCSD(T)	cc-pVDZ	2.92	2.88
	CCSD(T)	cc-pVTZ	3.11	3.05
Be_{26}	CCSD	cc-pVDZ	2.66	2.64
	CCSD(T)	cc-pVDZ	2.93	2.90
Mg_4	CCSD	cc-pVDZ	0.80	0.79
	CCSD(T)	cc-pVDZ	1.02	1.00
	CCSDTQ	cc-pVDZ	1.07	1.05
	CCSD(T)	cc-pVTZ	1.18	1.16
	CCSD(T)	cc-pVQZ	1.25	1.22
Mg_{13}	CCSD	cc-pVDZ	0.89	0.87
	CCSD(T)	cc-pVDZ	1.15	1.13
	CCSD(T)	cc-pVTZ	1.30	1.27
Mg_{26}	CCSD	cc-pVDZ	0.92	0.90
	CCSD(T)	cc-pVDZ	1.24	1.21

[a] HF and DFT bulk data used in eq 4 are: $E_b^{\mathrm{HF}} = 2.21$ (0.36) eV, $E_b^{\mathrm{LDA}} = 4.20$ (1.76) eV, $E_b^{\mathrm{GGA}} = 3.67$ (1.48) eV for Be (Mg).[13,27,30] Experimental values are 3.41 and 1.54 eV for Be and Mg, respectively.[26,27]

Table 3 presents results obtained with this kind of extrapolation, using various cluster sizes, n, for extracting $c(n)$ and applying either LDA or GGA E_b values in eq 4. Also, CCSD(T) correlation energies obtained with the cc-pVDZ basis for $c(n)$ in eq 3 are supplemented by CCSD and CCSDTQ energies and by values with larger basis sets, if available for a given n.

It is seen that the results are quite insensitive to the density functional used for extrapolation. Differences between LDA and GGA are ≤0.03 eV for Mg and ≤0.08 eV for Be for all cluster sizes $n \geq 4$. This is much smaller than the difference between the raw LDA and GGA data. (See Tables 1 and 2.) Of course, in the limit $n \rightarrow \infty$, the values should become independent anyway on whether LDA or GGA was used for extrapolation.

With respect to the cluster size dependence, we see that changes are moderate: differences between values extrapolated from $n = 4$ and 26 are ~0.1 eV for Be and ~0.2 eV for Mg. Also, the $n = 13$ values are not exceptional any more: they lie in between the $n = 4$ and 26 values. Therefore, the sensitivity of the extrapolated data to the cluster size is much more favorable than for those described in the previous paragraph.

The effect of triples in $E_b^{\mathrm{corr}}(n)$ for calibrating $c(n)$ in eq 3 turns out to be significant: without the triples, the calculated cohesive energies deteriorate by 0.2 to 0.3 eV. Inclusion of full triples and quadruples, on the other hand, enhances them by ~0.05 eV. About equally as important as triple excitations are basis-set effects: replacing cc-pVDZ by cc-pVTZ leads to an increase in the cohesive energy E_{coh} by 0.15 to 0.20 eV for Be and of ~0.15 eV for Mg, whereas going to cc-pVQZ enhances E_{coh} by another ~0.05 eV.

In comparison to the experimental cohesive energies, that is, 3.41 eV for Be and 1.54 eV for Mg, our CCSD(T)/GGA values

TABLE 4: Final Estimates of Bulk Cohesive Energies Per Atom (Electronvolts) Using the Extrapolated Values of Table 3[a]

	Be	Mg
CCSD(T)/GGA	2.90	1.21
+ basis-set corrections	3.15	1.47
+ higher excitations	3.19	1.52
exptl	3.41	1.54

[a] CCSD(T)/GGA values are taken from $n = 26$, basis-set corrections are taken from $n = 13$ and $n = 4$ (see text), and the effect of higher excitations is taken from $n = 4$. Experimental values (exptl) are taken from refs 26 and 27.

extracted from $n = 26$ (2.90 eV for Be, 1.21 eV for Mg) are too small by 0.5 and 0.3 eV, respectively. (See Table 4.) Adding the cc-pVDZ → cc-pVTZ basis effect from $n = 13$, the deviations from experiment are reduced to 0.3 and 0.2 eV, respectively. Further reductions by basis-set improvement toward the basis-set limit can be estimated from the $n = 4$ data to 0.1 eV (twice the cc-pVTZ → cc-pVQZ effect), and another 0.05 eV can be expected from the effect of higher excitations (also extracted from $n = 4$). A rough estimate of the cluster-size effect beyond $n = 26$ is also on the order of 0.1 eV. This would bring the extrapolated cohesive energies to within 0.1 eV of the experimental values.

This is a significantly more uniform accuracy than that reached with the incremental scheme for Be and Mg. There, values of 4.66 and 1.53 eV were obtained;[12,13] that is, the difference to experiment was 0.01 eV for Mg but 1.25 eV for Be. (Improvement is possible for Be but at the expense of calculating a large number of higher-order terms.[31]) The accuracy reached with the CCSD(T)/LDA and CCSD(T)/GGA extrapolations can also be compared with that obtained with standard LDA and GGA calculations for the infinite crystal. There, the deviations from experiment are 0.8 eV for Be and 0.2 eV for Mg (LDA), and the corresponding GGA deviations are 0.3 and −0.06 eV, respectively.

5. Conclusions

A hybrid Hartree−Fock/density-functional scheme has been used for extrapolating CCSD(T) binding energies per atom, E_b, for Be and Mg clusters to the bulk limit. It turns out that the results obtained are only weakly dependent on the cluster size used for extracting the CCSD(T) E_b values. However, the inclusion of triple excitations in CCSD(T) and the use of extended basis sets are instrumental for reaching agreement to 0.1 to 0.2 eV with the experimental cohesive energies of the Mg and Be metals.

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